The quality of streams, rivers, and ground water reflects complex interactions of natural and humaninduced conditions. Natural watershed scale factors such as climate, geography, and topography influence water chemistry and aquatic biological communities. Broadscale land uses, as well as localized human activities combine with background conditions to influence overall water quality.

Within ALMN, the interaction of a diverse geography and an equally diverse set of land uses influence the quality of the water resource. Surface-water sampling sites were selected in a variety of land-use settings including forest, urban, agriculture, mining, and mixed land use. The study design for ground water focused on assessing the water-quality conditions of major aquifers in ALMN, with emphasis on the quality of recently recharged ground water associated with ongoing and recent human activities (see page 22) (Gilliom and others, 1995). Specific findings from particular land uses and geographic settings are presented in the rest of this part of the report.

Coal Mining Dominates Water Quality

Although not easily represented on land-use maps, mining has the greatest influence on surface and ground-water quality and aquatic habitat of any single land use in ALMN. The area of surface mined land is difficult to quantify because of revegetation; deep-mine activity leaves virtually no trace on the surface.

Coal has been mined in ALMN for more than 200 years and has been central to the economy and lifestyle of many communities. Extensive commercial coal mining

began with almost no concern for the protection of the land surface and water resources. Consequently, stream-water quality in much of ALMN was severely degraded streams became virtually unusable and supported few aquatic species. Mine-related influences have long been recognized as among the most serious and persistent water-quality problems in Pennsylvania (Pennsylvania Department of Environmental Protection, 1996) and West Virginia (West Virginia Department of Environmental Protection, 1998), as well as throughout Appalachia, extending from New York to Alabama (Biesecker and George, 1966).

Surface and underground coal mining and coal-cleaning processes expose many elements to weathering. Pyrite and marcasite (iron disulfides also known as "fool's gold") are naturally occurring compounds commonly found in coal Nearly all basins greater than 100 square miles within the coal-bearing region of ALMN have been mined at one time or another, many with several coal-extraction techniques.

and in overburden rock. Pyrite is the major source of acid mine drainage (AMD) in the Eastern United States (Rose and Cravotta, 1998). During or after mining, AMD can be formed by a series of complex geochemical and bacterial reactions that occur when pyrite is exposed to air and water (Pennsylvania Department of Environmental Protection, 1999) (fig. 5). Through these reactions, some dissolved ferrous iron will precipitate out of solution in the form of insoluble ferric hydroxide (fig. 6).

Secondary reactions of the acidic water can bring into solution other constituents in the coal and the overburden rock, such as manganese, aluminum, zinc, arsenic, bar-

Pyrite + Oxygen + Water = Ferrous iron + Sulfate + Acidity

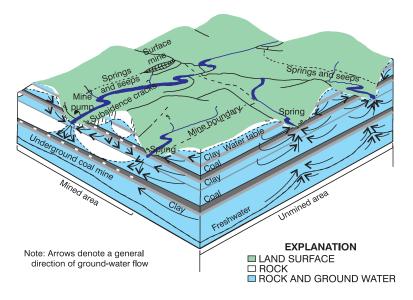


Figure 5. Coal mines disrupt existing flow patterns of ground water and surface water. Oxygen dissolved in surface water is transported to rock strata containing pyrite. Sulfuric acid is produced, which may then emerge in springs, seeps, and streams carrying large amounts of dissolved metals. (Figure adapted from Puente and Atkins, 1989.)



Figure 6. Reddish-orange iron precipitate is commonly seen in streams affected by acid mine drainage.

ium, cadmium, cobalt, copper, and silver. Some reach concentrations potentially dangerous to wildlife and may exceed drinking-water standards (table 1). These constituents are then subject to additional reactions (such as the formation of precipitates), are adsorbed onto sediments, or are taken up in the tissues of organisms (bioconcentrated).

Sulfate is an Indicator of Coal-Mining Activity

Coal-mine drainage can be acidic or alkaline and can seriously degrade both surface- and ground-water supplies. AMD, in which the acidity exceeds alkalinity, typically contains elevated concentrations of sulfate, iron, manganese, aluminum, and other dissolved material. In contrast, neutralized or alkaline mine drainage (NAMD) has an alkalinity that exceeds acidity; however, NAMD can still have elevated concentrations of sulfate, iron, manganese, and other constituents.

Dissolved trace elements are not generally reliable indicators of AMD or NAMD because they may not remain in solution. Sulfate, however, is a reliable indicator of mine drainage because sulfate is highly soluble and chemically stable at the pH levels normally found in natural waters (Hem, 1985).

The U.S. Environmental Protection Agency (USEPA) has established a Secondary Maximum Contaminant Level (SMCL) of 250 mg/L (milligrams per liter) for sulfate. SMCLs are applied to public water supplies and are nonenforceable levels for contaminants that may affect the taste, odor, or appearance of water. High sulfate concentrations in water may cause diarrhea in sensitive populations (U.S. **Environmental Protection** Agency, 1999a).

The amount of a constituent carried out of a stream system is called the yield. Sulfate yields were, on average, 5 times greater in stream basins where mining has occurred than in unmined basins sampled monthly in 1997–98 (fig. 7). With one exception (Stonycreek River), yields of dissolved iron and dissolved manganese were similar in mined and unmined basins.

The Stonycreek River had the highest sulfate yield of the 11 sampled streams and is considered to be highly degraded by AMD, primarily from abandoned mines.

Table 1. Regional background concentrations of constituents influenced by mine drainage were estimated by using the 90th percentile for each constituent from streams unaffected by mining

[USEPA, U.S. Environmental Protection Agency, mg/L, milligrams per liter; --, not calculated; μg/L, micrograms per liter]

Selected mining constituents ¹	USEPA Secondary Maximum Contaminant Level	Regional back- ground concentra- tion	
Dissolved solids	500 mg/L		
рН	6.5–8.5	7.0	
Sulfate	250 mg/L	20.8 mg/L	
Iron	300 μg/L	129 μg/L	
Manganese	50 μg/L	81 μg/L	
Aluminum	50-200 μg/L	23 μg/L	

¹Other coal-mining-related constituents include alkalinity and acidity.

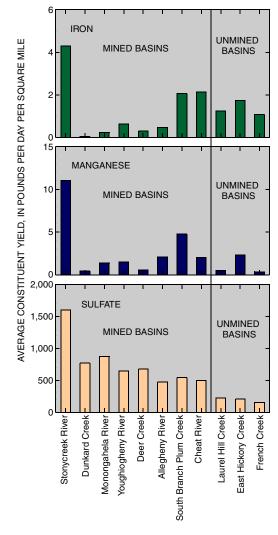


Figure 7. Sulfate is a more stable indicator of mine activity than dissolved iron or manganese.

Currently, efforts are being made to restore the water quality in this river, mainly through the construction of passive treatment systems to treat abandoned-mine discharges inventoried in 1992-95 (Williams and others, 1996). Since 1995, about \$3.5 million has been spent on mine-drainage remediation projects throughout the Stonycreek River Basin, resulting in the removal of iron, aluminum, and acidity from the Stonycreek River at a rate of 111, 133, and 1,192 tons per year, respectively (D. Seibert, Natural Resources Conservation Service, oral commun., 2000). A similar study to identify mine discharges was completed in a Monongahela River tributary, the Cheat River (Williams and others, 1999).

Aquatic Communities are Affected in Streams Receiving Large Amounts of Mine Drainage

Streams receiving mine drainage may range from supporting diverse communities of aquatic life to being lethal to many organisms, depending on a variety of factors. The ecological setting of a stream can affect the types and rates of water-quality changes in response to human influences. Ecoregions and basin size are two factors that relate to differences in aquatic communities. Ecoregions are used to group areas that are ecologically similar and can be expected to have similar aquatic communities. ALMN is divided into six ecoregions (fig. 8), five of which were included in the sampling design in ALMN. Basin size affects species diversity because larger basins tend to have a greater variety of habitats available.

The fish community was sampled at 11 sites in ALMN, 7 of which received mine drainage. A difference in fish abundance and number of fish species was evident between streams in mined basins compared to those in unmined basins. None of the streams sampled had a depressed pH (less than 6.5). In the Central Appalachian Ecoregion, at Stonycreek River, only 2 species (2 individuals) were captured, whereas in Laurel Hill Creek, a similar stream in a nearby unmined area, 16 species (384 individuals) were captured. Where basin sizes were comparable, the presence or absence of coal mining in a basin was evident in some aspects of the fish-community structure (fig. 9).

Few organisms can tolerate even brief periods of acidic or mineralor silt-laden water. Episodic events or chronic conditions that result in concentrated AMD entering a stream are obvious and result in a nearly complete loss of aquatic species, such as in Stonycreek River. The effects are often more subtle in streams receiving NAMD, where species sensitive to sedimentation, trace-element concentration, or hydrologic changes are affected (Letterman and Mitsch, 1978). In a regional study between ALMN and the Kanawha-New River Basin, 61 sites were sampled for aquatic invertebrates (insects, worms, crustaceans, and mollusks) and water chemistry during a low-flow period in 1998. At sites where sulfate con-

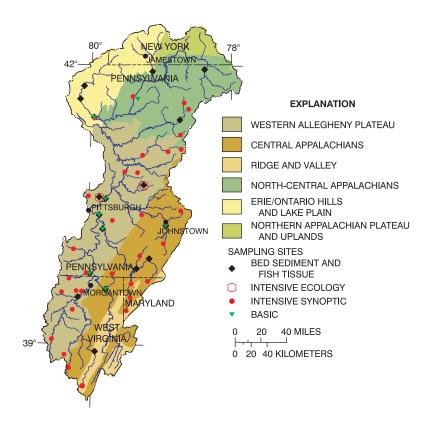


Figure 8. Assessments of the health and condition of aquatic life and habitat focused on four of the six ecoregions represented on this map. Contaminants associated with bed sediment and tissue were analyzed at 19 sites. (Ecoregions from Omernick, 1987)

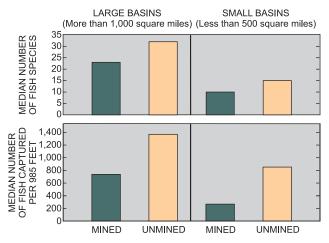


Figure 9. The number of fish species and the number of individual fish captured per 985-feet stream reach was greater at unmined sites than at mined sites of comparable size.

centrations were greater than the estimated background level, decreasing diversity was noted for three groups of sensitive insect species (mayflies, stoneflies, and caddisflies), although pH was 6.5 or greater at all these sites. (See fig. 23 on page 21.)

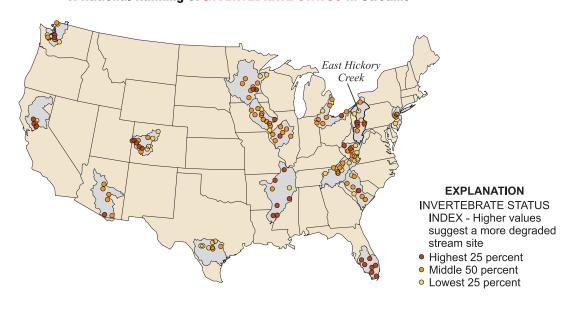


INVERTEBRATE INDEX STATUS IS AMONG THE BEST IN THE NATION IN FORESTED SETTINGS

Aquatic life in stream systems where human influence is minimal generally represents a more natural community than in streams strongly influenced by human activity. These sites can be used to define background (reference) conditions that are helpful in interpreting how various land uses change the types and numbers of organisms living downstream. NAWQA examines fish, invertebrate, and algal communities and uses indices based on reference sites as part of assessing water quality. For example, an invertebrate status index (T.F. Cuffney, U.S. Geological Survey, written commun., 2000) averaged 11 invertebrate-community measures (metrics) used to indicate various aspects of the life cycles of the organisms assessed. This index can be used to make relative comparisons between sites sampled by NAWQA.

An ALMN site, East Hickory Creek near Queen, Pa., whose basin is more than 95-percent forested, had the best quality (lowest invertebrate index score) nationally of 140 sites sampled between 1996 and 1998 (Appendix). In contrast, streams in either urban or coal-mine settings ranked among the highest 25 percent of those sampled.

A National Ranking of INVERTEBRATE STATUS in Streams



Ground-Water Quality is Affected Near Mined Areas

During 1996–98, 45 domestic water-supply wells were sampled in ALMN in the high-sulfur coal region of the Appalachian coal fields (Tully, 1996). Water samples were collected from 30 of the 45 wells within about 2,000 feet and hydrologically downgradient (downhill in this area) from a reclaimed surface coal mine. The additional 15 wells are in areas believed to be unmined.

Analysis of ground-water data indicates that surface coal mining continues to affect ground-water quality after all mining and reclamation has ceased. Several constituents related to mine drainage exceeded the USEPA SMCL more frequently in water sampled from wells downgradient from reclaimed surface coal mines than in well water from unmined areas.

Sulfate concentrations exceeded the USEPA SMCL for sulfate (250 mg/L) at 20 percent of domestic wells sampled in mined areas but at no wells sampled in unmined areas. Iron concentrations at wells near mined areas exceeded the SMCL (300 µg/L [micrograms per liter]) in 60 percent of the wells, compared to 20 percent of wells in unmined areas. Similarly, manganese concentrations exceeded the SMCL (50 µg/L) in 70 percent of wells from mined areas compared to 47 percent of wells in unmined areas. Finally, samples from 20 percent of the wells in mined areas exceeded the SMCL for total dissolved solids, whereas samples from only 7 percent of the wells in unmined areas exceeded the SMCI.

Concentrations of mine-related constituents, such as sulfate, iron,

manganese, and dissolved solids can exceed SMCLs for drinking water in unmined areas because of the geologic setting (mostly rocks of Pennsylvanian age that can contain high concentrations of iron and manganese). High concentrations of sulfate in ground water of the Appalachian coal fields, however, usually indicates that coal has been mined nearby or in a location hydrologically upgradient from the sample location. Current regulations do not require treatment of mine-discharge water for sulfate. Discharge water is generally regulated and treated to reduce concentrations of iron and manganese and to maintain pH in the range of 6.5 to 8.5 units.

Concentrations of Trace Elements in Bed Sediment Exceed Aquatic-Life Guidelines

Trace elements typically are present in surface-water systems in small amounts. Local geologic conditions or land-use activities can increase the concentration of some elements to levels that may impair aquatic life or limit water use. Trace elements may be dissolved in water, bound to sediments, or incorporated into the tissues of organisms, depending on the chemical properties of each element. In ALMN, several trace elements in addition to zinc and chromium were detected at high concentrations in bed sediment or tissues (Appendix).

Arsenic is a trace element that is potentially damaging to both human health and aquatic life. Increased arsenic concentrations can result from human activity, such as application of pesticides or the combustion of fossil fuel, or from natural weathering of arsenic-

bearing rock (Ferguson and Gavis, 1972). Arsenic was detected at concentrations above the estimated background concentration of 5.9 µg/g (micrograms per gram) (Canadian Council of Ministers of the Environment, 1995) at all 50 bed-sediment sites sampled between 1996 and 1998 in ALMN. The Probable Effect Level (PEL) for arsenic in bed sediment of 17 μg/g (Canadian Council of Ministers of the Environment, 1995) was exceeded at 12 of 50 sites, where concentrations ranged from 18 to 52 $\mu g/g$.

Land use did not appear to be a factor in the arsenic concentrations observed in ALMN, although atmospheric deposition cannot be ruled out. Each of the sites in ALMN where the PEL was exceeded, with the exception of Stonycreek River (a heavily mined basin), were distributed in the northern, once glaciated part of the Allegheny River Basin. Glacial action during the last ice age broke up and moved near-surface rock, exposing this rock to weathering and releasing some arsenic (Welch and others, 1988).

In contrast, concentrations of some other trace elements in ALMN appear to be related to land use. Concentrations of cadmium, copper, chromium, lead, mercury, and zinc each exceeded the PEL aquatic-life guidelines in bed-sediment samples at least once in samples from mined or mixed-land-use sites.

Concentrations of cadmium in whole-fish samples, for which no guidelines exist, are among the highest sampled by NAWQA during 1995–98. Several trace elements (such as nickel) that also have no established guidelines for either bed sediment or tissue are



TRACE ELEMENTS MAY LIMIT AQUATIC LIFE IN URBAN STREAMS AND MINED AREAS

The acidity of some mine drainage may dissolve and subsequently transport large amounts of trace elements from exposed rock. These trace elements, often found naturally in small amounts, can accumulate in streambed sediments. Trace elements, low levels of which are required by organisms, can reach toxic concentrations when concentrated in food, water, or sediments.

Aquatic-life guidelines, used as a reference level, are based on Environment Canada's guideline (Canadian Council of Ministers of the Environment, 1995) and have no regulatory force in the United States. Zinc and chromium were found at all bed-sediment sampling sites in ALMN, and at the 50 sites sampled, the aquatic-life Probable Effects Level (PEL) for zinc (315 $\mu g/g$) and chromium (90.0 $\mu g/g$) was exceeded at 15 and at 5 sites, respectively (Appendix). Eleven bed-sediment samples from ALMN had zinc concentrations among the highest 10 percent nationally of samples analyzed by NAWQA since 1991. PELs were most often exceeded in areas subjected to industrial or mining land use in ALMN.

Zinc, along with other trace elements that exceed aquatic-life guidelines, may contribute to degradation of aquatic communities in streams. Some sites in ALMN were among the most degraded sites nationally for aquatic invertebrates (Appendix).

National indicators for invertebrate status (Appendix) with zinc and chromium concentrations in bed sediment, in micrograms per gram of sediment

Stream name and location	Predominant land use	Invertebrate status	Zinc	Chromium
French Creek at Utica, Pa.	Mixed	•	120	58
East Hickory Creek near Queen, Pa.	Forested	•	190	63
South Branch Plum Creek at Five Points, Pa.	Agriculture	•	130	82
Deer Creek near Dorseyville, Pa.	Urban	•	170	88
Dunkard Creek at Shannopin, Pa.	Mining	•	190	88
Youghiogheny River at Sutersville, Pa.	Mixed	•	410	87
Stonycreek River at Ferndale, Pa.	Mining	•	700	90
Monongahela River at Braddock, Pa.	Mixed	•	510	110
Allegheny River at New Kensington, Pa.	Mixed	•	330	120

- lowest 25 percent nationally (Least-degraded sites)
- middle 50 percent nationally
- highest 25 percent nationally (Most-degraded sites)

elevated in mixed-land-use settings (Appendix).

Water Quality of the Large Rivers of the Allegheny and Monongahela River Basins is Improving

The large rivers sampled in ALMN are important for their envi-

ronmental and esthetic qualities, as well as sources for drinking water. Sections of the upper Allegheny River are designated federally as Scenic Rivers (Pennsylvania Department of Conservation and Natural Resources, 2000). French Creek, a tributary of the Allegheny River, supports several State and

federally protected endangered species (see page 12) and is an important stream nationally for the protection of aquatic species (Masters and others, 1998). Whitewater rafting on the Youghiogheny and Cheat Rivers is a thriving recreational industry.

The water quality in a river that drains large areas integrates water potentially influenced by a broad range of natural and human factors. The industrial and resource extraction land-use history in ALMN previously resulted in poor water quality in some rivers and streams. Early in the 1900s, fish were rarely found in the lower Allegheny and Monongahela Rivers and then only during high flows, when river water was diluted by surface runoff. Cravfish also were rare, and freshwater mussels had been eliminated (Ortmann, 1909). Ortmann described lower reaches of Monongahela River tributaries, the Cheat River and Youghiogheny River, as degraded by mine drainage. As recently as the mid-1960s, fish surveys on the Monongahela River found zero to four fish species (U.S. Army Corps of Engineers, 1976).

The Allegheny River and
Monongahela River sites sampled in this study have been sampled comparably under various

USGS programs since the early 1970s, permitting a general comparison of water-quality conditions since that time.

A measure of the acidic and basic properties of natural waters is pH. The pH of source water is useful for determining water-treatment

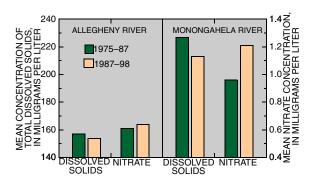


Figure 10. For the two 12-year periods examined, the Allegheny and Monongahela Rivers improved in some water-quality respects (MCL, Maximum Contaminant Level; SMCL, Secondary Maximum Contaminant Level).

options and evaluating the suitability for support of aquatic plants and animals. Natural factors, such as rock types in a basin, can affect pH, as can industrial discharges and mine drainage. As recently as the 1960s, the Monongahela River was occasionally too acidic (low pH) to support a diverse aquatic community (Finni, 1988). Since the early 1970s, the median pH at the NAWQA sampling sites increased from 7.0 in the period 1975 to 1987 to 7.4 in the period 1987 to 1998 in the Allegheny River. During the same periods, the median pH increased from 7.0 to 7.6 in the Monongahela River. Although this represents an overall increase in pH for both sites, about 1 percent of the samples collected from these two sites had pH values that were lower than the minimum aquaticlife water-quality guideline of 6.0 (Pennsylvania Department of Environmental Resources, 1984) during the period 1987 through 1998. For organisms living in these rivers, occasional periods when the pH is either too high or too low can be lethal for a particular species.

The concentration of dissolved solids in a water body can be increased as a result of industrial or municipal wastes, drainage from mines or oil fields, or drainage from agricultural land. Median concentrations of dissolved solids have decreased at the Allegheny and Monongahela River sampling sites over the last 25 years. Dissolved-solids concen-

trations have decreased by 2 percent in the Allegheny River and by 6 percent in the Monongahela River. Reductions in dissolved solids in the Monongahela River have virtually eliminated the exceedences of the SMCL of 500 mg/L (fig. 10).

Elevated nitrate concentrations can result in increased plant and algal growth (U.S. Geological Survey, 1999a), which can, in turn, alter the taste of water and affect other aquatic life. Nitrate increases can be related to some of the same sources as dissolved solids, including both point-source discharges, such as industrial wastewater discharges and sewage, or nonpoint sources, including atmospheric deposition and agricultural fertilizer use (U.S. Geological Survey, 1999a). In contrast to dissolved solids, however, median nitrate concentrations have increased by 3 percent in the Allegheny River and by 25 percent in the Monongahela River. Nitrate, which contains nitrogen, can be converted to other nitrogen-containing compounds relatively easily. Total nitrogen was not routinely measured in early studies. The increase observed in

nitrate may be partly the result of changes in the form of nitrogen in the rivers, typically due to sewage-treatment-plant upgrades (U.S. Geological Survey, 1999a).

The general improvement in water quality described above in sections of the Allegheny and Monongahela Rivers has been accompanied by an increase in the number and species diversity of fishes. A sample of the fish community at the Monongahela River site in 1998 contained more than 1,100 individual fish representing 12 species. This included many sport fish such as smallmouth bass and sauger. Species richness was even greater in the Allegheny River, which had 21 species, again including many sport fish as well as species sensitive to pollution, such as redhorse sucker. Significantly, the silver chub, Macrhybopsis storeriana, a minnow that had not been seen in these rivers since the late 1800s (Cooper, 1983), was captured in both 1997 and 1998. The recovery of rare species is a further indication of the degree of improvement in water quality in these river segments.

Persistent Pesticides and PCBs were More Prevalent in Fish Tissue than in Sediment

Numerous synthetic organic compounds have been manufactured to fulfill various needs of society. These compounds have a range of stability in the environment. Some break down rapidly, whereas others can be highly stable and persistent. Some stable synthetic organic compounds are no longer in use in the United States.

Organochlorines in this group are commonly soluble in fat or can bond to particles in the water and settle out. Some bioconcentrate in

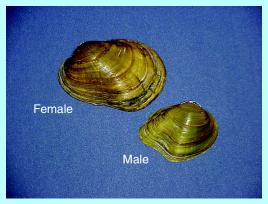
Grass-roots efforts seek to protect water quality and aquatic life

Many of the water-quality issues receiving national attention arise from landscape-scale activities known as nonpoint sources. Managing nonpoint sources often requires the cooperation of many people living in a river basin.

Watershed groups have been formed by citizens concerned with the conditions in local waterways. Nationally, as well as in ALMN, these groups are increasingly important. Many include partnerships with conservation groups and government agencies.

Many watershed organizations in ALMN are working to improve degraded streams. In contrast, several local groups are actively working to keep their resource in good condition. French Creek is an example of a stream that has maintained high water quality and whose citizens are working to maintain this

resource. This creek, and its associated ground water, supply drinking water to many homes, municipalities, and industries. French Creek also boasts the greatest number and variety of fish. invertebrates, and aquatic plants in ALMN. Many of these species are categorized as endangered by State and Federal governments. Several are found nowhere else in ALMN and at very few other places in the world (see photograph at right). These rare, sensitive species and the high overall species diversity in French Creek are evidence of the high quality of the water and stream habitat in this basin.



Northern riffleshell is a globally endangered species doing well in French Creek and sections of the Allegheny River. Two-thirds of related native North American freshwater mussels are now rare or endangered. These animals are indicators of exceptional stream quality.

fat, reaching higher concentrations in organisms than in the environment. They can accumulate in predators that eat contaminated organisms. In the tissues of animals, these compounds can have a variety of effects including toxicity, reproductive impairment, or cancer. Whole fish from 16 sites in ALMN were analyzed for 28 organochlorine compounds. Streambed sediment was analyzed for 32 compounds at these same 16 sites plus an additional 3 sites (fig. 8). At the sites where both fish and bed sediment were sampled, those compounds detected in both media were present at higher concentrations in fish tissue than in the sediment (Appendix).

Although use of PCBs was discontinued in the United States in the 1970s. PCBs were detected in whole-fish tissue samples at 10 of 16 sites in 1997. This mixture of compounds was detected at only 4 of 19 sites in streambed sediment. Those sites at which PCBs were below the detection level in fish tissue were in basins dominated by agriculture or forest. Fish-tissue samples from eight sites with mixed land use had total PCB concentrations above the guideline for protection of fish-eating wildlife (Newell and others, 1987).

DDT and chlordane use has been discontinued in the United States since the 1970s. DDT and its breakdown products were detected in fish at 15 of 16 sites and in sediment at 9 of 19 sites. Only at the Allegheny River at New Kensington, Pa., however, did the concentration of total DDT in fish samples exceed the guideline of 200 mg/kg (micrograms per kilogram) established to protect fish-eating wildlife. Chlordane was detected in 11 of 16 whole-fish samples and in 4 of 19 streambed-sediment samples. The guideline of 500 mg/kg for total chlordane (which also includes breakdown products) for protection of fish-eating wildlife was exceeded in fish samples only at the Monongahela River near Braddock, Pa.

Public-health advisories are in place to restrict consumption or prohibit taking of several fish species from certain sections of the Allegheny and Monongahela Rivers because of PCB and chlordane contamination (Pennsylvania Fish and Boat Commission, 1999). These compounds are relatively stable, are apparently being cycled between aquatic life and bed sediment, and may persist in ALMN for many more years.

Low Concentrations of Numerous Pesticides were Detected in an Agricultural Stream and an Urban Stream

Two basins of similar size were chosen to assess the occurrence and distribution of a broad range of pesticides under different streamflow conditions. The Deer Creek Basin represented a predominantly residential/urban setting, and the South Branch Plum Creek Basin represented a predominantly agri-

cultural setting (Williams and Clark, 2001).

Of the 84 pesticides and pesticide metabolites (breakdown products) in this analysis, 25 were detected at least once in Deer Creek and 20 were detected at least once in South Branch Plum Creek. Some pesticides show a seasonal pattern in water samples from both streams (fig. 11).

All detectable pesticide concentrations from both streams were less than drinking-water-quality guidelines or standards (table 2). However, the maximum measured concentrations of diazinon in Deer Creek (0.097 μ g/L) and South Branch Plum Creek (0.094 μ g/L) exceeded the water-quality guideline to protect aquatic life of 0.08 μ g/L.

Prometon is the most commonly detected herbicide in surface water and ground water in urban areas

A note on National biological status scores

Although water-quality guidelines for the protection of aquatic life were exceeded for several of the pesticides detected in ALMN, there is no indication that the concentrations have been lethal to the organisms in these streams. National invertebrate and algal scores indicate that these biological communities have not been degraded and are comparable to those at a forested site in ALMN (Appendix). The national fish status score, although indicating that the urban and agricultural setting have better quality fish communities than the forested site, places considerable emphasis on non-native fish species. The forested site is stocked with non-native trout to supplement sport fishing. Abundant non-native fish populations are an indicator of human influence and may point to habitat or water-quality degradation in other situations.

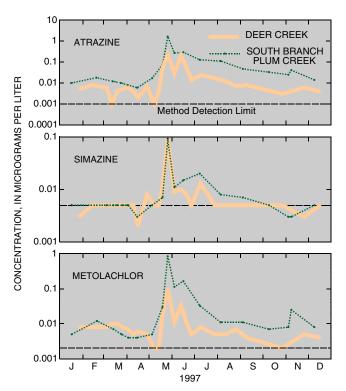


Figure 11. A distinct seasonal pattern is evident in the concentrations of atrazine, simazine, and metolachlor. The peak concentrations of these three pesticides coincide with herbicide-application periods and increased spring rainfall. (Concentrations below the method detection limit are believed to be reliable detections but with greater than average uncertainty in quantification.)

(Capel and others, 1999). It is used as a preemergent herbicide to control vegetation on bare ground around buildings and fences, along rights-of-way, and in conjunction with the application of asphalt. Prometon was detected in 90 percent of the samples collected in Deer Creek. The highest measured concentration was 0.355 µg/L in the first of five storm samples collected on August 25-26, 1998. That concentration was more than 10 times the maximum measured concentration in 1997 but is still well below the drinking-water-quality guideline of 100 µg/L. No prometon guidelines have been established for the protection of aquatic life.

The insecticide diazinon is commonly used in homes, gardens,

parks, and commercial areas. Detections of diazinon from samples collected in Deer Creek in 1997 showed no seasonal pattern; however, five of the seven detections were in samples collected shortly after a peak in streamflow due to overland runoff.

The aquatic-life water-quality guideline for carbaryl of 0.2 µg/L was exceeded in four of the five stormflow samples collected in Deer Creek on August 25–26, 1998.

Pesticides are at Low Concentrations when Detected in Ground Water

Ground-water samples from 58 shallow domestic wells throughout ALMN were analyzed for pes-

Table 2. Many pesticides are in widespread use for the control of insects (insecticides) or plants (herbicides). Pesticides may be sold under a variety of names, depending on the manufacturer (Table adapted from U.S. Geological Survey, 1999b)

Γιια/T	micrograms	nor liter	NIA	not	ovoiloblo]	
μg/L,	micrograms	per mer.	INA,	not	available	

Pesticide name	Trade name	Use	Drinking-water- quality guidelines or standards (µg/L)	Aquatic-life water-quality guideline (µg/L)
Atrazine	AAtrex, Atrex, Atred, Gesaprim	Herbicide	31	1.8
Diazinon	Basudin, Diazatol, Neocidol, Knox Out	Insecticide	.6	.08
Dieldrin	Panoram D-31, Octalox, Compound 497, Aldrin epoxide	Insecticide	.02	.056
Carbaryl	Carbamine, Denapon, Sevin	Insecticide	700	.2
Metolachlor	Dual, Pennant	Herbicide	70	7.8
Prometon	Pramitol, Princep, Gesagram 50, Ontracic 80	Herbicide	100	NA
Simazine	Princep, Caliber 90, Gesatop, Simazat	Herbicide	4 ¹	10

¹Drinking water-quality standard (Maximum contaminant level).

ticides. One to five pesticide compounds were detected in 34 percent of the samples. Nine different compounds were detected at concentrations ranging from less than 0.001 to $0.17 \mu g/L$. All detections were at or below the methoddetection limit. No compounds were detected above drinking water-quality guidelines or standards. The five most frequently detected compounds were the agricultural herbicides atrazine, metribuzin, and metolachlor; the insecticide diazinon; and a breakdown product of atrazine, deethylatrazine.

Of the 58 ground-water samples analyzed for pesticides, 30 samples were from wells in valley-fill aquifers and 28 samples were from fractured-rock aquifers (see page 22). Forty percent of the samples from valley-fill aquifers and 29 percent of the samples from fractured-rock aquifers contained at least one pesticide compound. Deethylatrazine was the only pesticide detected in more than 30 percent of all samples in the valley-fill aquifers. No pesticides were detected in more than 22 percent of

sampled wells in the fractured-rock aquifers.

Nine different pesticide compounds were detected in 12 samples from the valley-fill aquifers (fig. 12). The top four detected

compounds in samples from valley-fill aquifers were deethylatrazine, atrazine, metribuzin, and diazinon. Two or more pesticide compounds were detected in 20 percent of the samples in the valley-fill aquifers.

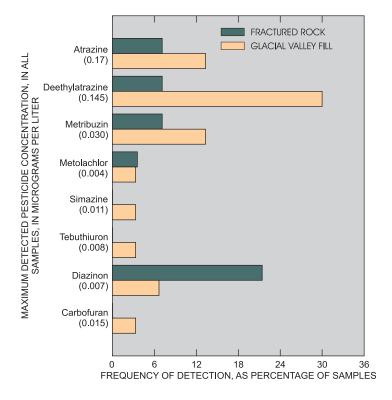
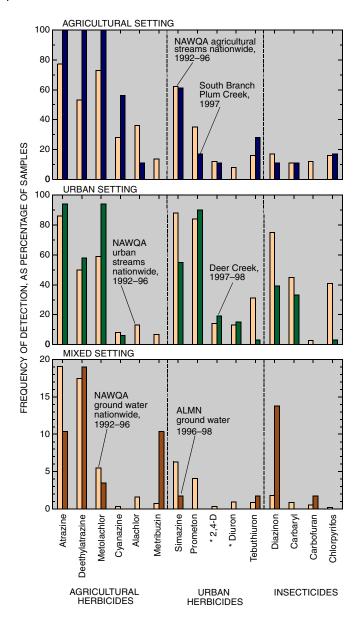


Figure 12. With exception of diazinon, pesticide-detection frequencies in ground water were higher in the valley-fill aquifers than in the fractured-rock aquifers. (Not shown above is the herbicide EPTC detected in a single sample— $0.004 \mu g/L$.)

PESTICIDES IN THE ALLEGHENY AND MONONGAHELA RIVER BASINS ARE SIMILAR TO THOSE DETECTED NATIONALLY

The commonly detected pesticides in South Branch Plum Creek, an agricultural basin, and in Deer Creek, an urban basin, were similar to the 15 most commonly detected pesticides in streams in NAWQA studies during 1992–96. The compounds detected in ground water from wells set in both valley-fill aquifers and fractured-rock aquifers are also among those most frequently detected in mixed landuse aquifers nationwide.



*Ground-water samples were not analyzed for the herbicides 2,4-D and Diuron in the Allegheny and Monongahela River Basins.

The most frequently detected mixture of compounds was atrazine (or the metabolite deethylatrazine) and metribuzin, detected in 10 percent of samples from the valley-fill aquifers.

Five different pesticide compounds were detected in the samples from the fractured-rock aquifers (fig. 12). The four most frequently detected compounds in samples from the fractured-rock aquifers were diazinon, deethylatrazine, atrazine, and metribuzin. Two or more pesticide compounds were detected in 14 percent of the samples in the fractured-rock aquifers. The most frequently detected mixture of compounds was metribuzin and diazinon, found in 7 percent of the samples from fractured-rock aquifers.

The higher detection frequency of pesticides in the samples from the valley-fill aquifers is most likely a result of greater vulnerability to pesticide contamination due to permeability of aquifer material and contaminant availability (Lindsey and Bickford, 1999). Both aquifers have similar contaminant-availability ratings; however, the valley-fill aquifers consist of unconsolidated sediments and are more permeable than the fractured-rock aquifers.

Volatile Organic Compounds were Detected at Low Concentrations in an Urban Stream

Volatile organic compounds derived from substances commonly used in residential and urban areas, such as gasoline and cleaning solvents, were detected in 24 of the 25 samples collected from Deer Creek (Pittsburgh metropolitan area) in 1997–98. Of the 87 VOCs

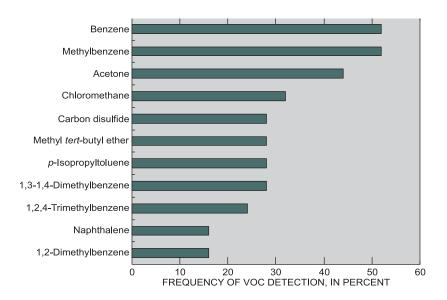


Figure 13. Of 87 VOCs analyzed for, 22 were detected in Deer Creek at Dorseyville, Pa. The 11 most frequently detected VOCs are shown.

analyzed for, 22 VOCs were detected at least once, and 55 percent of those detected were gasoline-related compounds (fig. 13). All measured concentrations of VOCs were well below drinkingwater standards and guidelines.

The occurrence of benzene, methylbenzene, methyl *tert*-butyl ether (MTBE), 1,3-1,4-dimethylbenzene, and naphthalene showed

evidence of seasonality in samples collected in 1997. All five compounds were detected in samples collected in February, November, and December, but were absent in samples collected in July, August, and September (fig. 14). Water temperature is a significant factor affecting the concentration and detection of VOCs. VOCs are more likely to be stable and

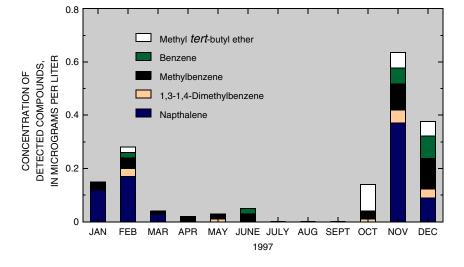


Figure 14. Volatile organic compounds were detected most often and at highest concentrations in surface-water samples in cool seasons (data from Deer Creek at Dorseyville, Pennsylvania).

detectable in cold water than in warm water. Warm temperatures tend to cause VOCs to be driven into the atmosphere. VOC concentrations in water can increase by a factor of about 3 to 7 when water temperatures decrease from 25°C (Celsius) to 5°C (Lopes and Bender, 1998).

VOCs can accumulate on impervious surfaces and can be flushed into the receiving stream during storms. Data from five storm samples collected in Deer Creek on August 25–26, 1998, showed that the maximum measured concentrations of acetone, carbon disulfide, benzene, 1,2,4-trimethylbenzene, and *p*-isopropyltoluene in a sample were collected as streamflow increased. The lowest concentrations were observed in the last samples collected as the stream receded. The concentration pattern demonstrates a flush-off effect as rains washed VOCs from the land surface to the stream (fig. 15).

Fourteen VOCs detected in a sample collected on December 10, 1997, may have resulted from a flush of accumulated VOCs from impervious surfaces in addition to a low water temperature (5.0°C). Of the 14 VOCs detected, 10 were gasoline-related compounds.

Low Levels of Volatile Organic Compounds were Detected in Most Domestic Wells Sampled

Of the 95 domestic wells throughout ALMN from which samples were collected for VOC analysis, at least one compound was detected in each of 87 samples (92 percent). A total of 28 different compounds were detected overall. Most samples (60 percent) contained two or more VOCs at detect-

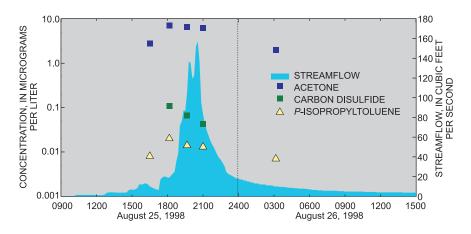


Figure 15. At Deer Creek, some VOCs are rapidly transported to streams during storms. These tend to become most concentrated before the floodwaters peak and decline before water returns to prestorm levels.

able levels, and one sample contained seven different VOCs.

All VOC detections were at low concentrations. Twelve VOCs were detected at concentrations at or above $0.1~\mu g/L$, including the four most frequently detected compounds (fig. 16). Of the 28 detected VOCs, drinking-water standards have been established for 20. None

of the VOCs detected exceeded established drinking-water standards or guidelines.

Thirty of the water samples analyzed for VOCs were from wells downgradient from recently reclaimed surface coal mines (mined sites), and 15 of the water samples were from wells in areas underlain by coal but undisturbed

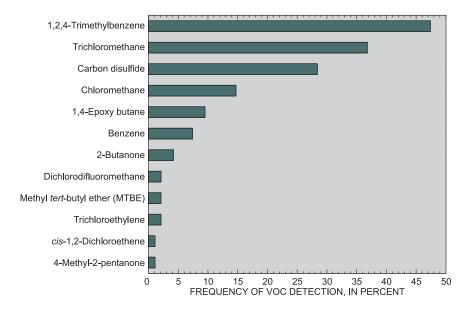


Figure 16. VOCs detected in ALMN ground water at concentrations greater than 0.1 microgram per liter.

by mining (unmined sites). Perhaps as a result of mine machinery use, fuel spills, or adjacent land use, gasoline-related compounds (1,2,4-trimethylbenzene, benzene, methylbenzene, and ethylbenzene) were detected more frequently and at higher concentrations in the samples collected from the mined sites, where these compounds were detected in 29 of 30 samples, compared to 9 detections in 15 samples from unmined sites.

Nitrate is Common in Streams and Ground Water

Nitrate is a nutrient that can affect water used either as a drinking source or as a medium for aquatic life. Nitrate is present naturally in surface water, but elevated concentrations can result in abundant algal growth and toxicity to some aquatic organisms. In well water, nitrate can be a significant health risk at high concentrations. The use of commercial and organic fertilizers and the combustion of fossil fuels has been linked to elevated nitrate concentrations in streams and shallow ground water nationwide (U.S. Geological Survey, 1999a).

In ALMN, 10 stream sites and 95 domestic wells were sampled for nitrate. Samples were collected monthly at the stream sites and once at each well during the period October 1995 through September 1998. Nitrate was detected in all surface-water samples and in 62 percent of ground-water samples. Among wells and streams, only one sample exceeded the USEPA MCL for nitrate in drinking water. The sample was collected from a domestic well in an agricultural setting. The highest median concentration of nitrate in wells and streams was in a stream



Figure 17. Livestock in South Branch Plum Creek, as in many agricultural basins, contribute nitrate to the ecosystem.

in an agricultural setting, South Branch Plum Creek (fig. 17).

The role of land use on the observed nitrate concentrations was investigated by comparison

Why is nitrate important?

Nitrate is the primary form of nitrogen dissolved in streams and ground water. Nitrate forms naturally in soil from transformations of nitrogen, nitrogen-based fertilizers, and manure.

Nitrate is the most widespread contaminant in ground water. Because most ground water eventually discharges to streams, the nitrate in ground water can pose a potential threat to surface-water quality. Surface runoff in areas where commercial fertilizers are used, as well as discharges from wastewater treatment facilities, can also contribute nitrate to streams.

Human ingestion of water with nitrate concentrations in excess of the MCL (10 mg/L as nitrogen) can lead to methemoglobinemia, or "blue-baby syndrome," a sometimes fatal blood disorder in infants.

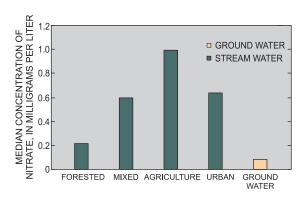


Figure 18. Median concentrations of nitrate in streams were higher than those found in ground water.

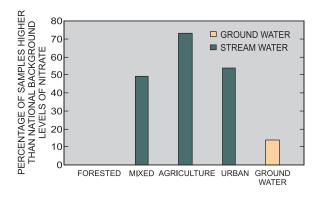


Figure 19. Streams in agricultural areas had the highest percentage of samples that exceeded national background levels for nitrate (0.6 milligrams per liter in streams and 2.0 milligrams per liter (U.S. Geological Survey, 1999a) in shallow ground water).

with a national background concentration for nitrate. The background concentration was estimated from samples collected in undeveloped areas (U.S. Geological Survey, 1999).

Nitrate concentrations in surface-water samples from forested areas in ALMN were less than national background concentration. Among other land uses with potential nitrate sources, concentrations of nitrate often exceeded the background level (figs. 18 and 19).

Activities typical of agriculture and urban/residential land use can lead to an increase in nitrate concentrations. Seasonal fertilizer applications, animal waste, and sewage are common sources of nitrate. Of the sampled streams in ALMN, 73 percent of samples from a stream draining an agricultural area exceeded background nitrate concentrations. In more populated areas (population density greater than 150 people per square mile), 54 percent of stream samples had nitrate concentrations that exceeded background concentrations.

Overall, streams in basins that integrate various land uses within ALMN had lower concentrations of nutrients than those dominated by either dense population or agriculture. Areas with both high population density and significant agricultural acreage exceeded background nitrate concentrations in 49 percent of stream samples.

Ground-water samples analyzed for nitrate were collected from wells in areas of mixed land use. Consequently, no agricultural-urban comparisons could be made for nitrate in ground water.

Radon in Ground Water is Common but Highly Variable

Radon is a radioactive gas that is produced naturally in rocks and soils as an intermediate product in the decay of uranium-238. Radon in ground water originates from nearby soil and rock and is a potential contributing source of radon in indoor air. Exposure to airborne radon has been identified by the U.S. Surgeon General as the second leading cause of lung cancer in the United States. About 20,000 deaths per year in the United States are attributed to airborne radon (U.S. Environmental Protection Agency, 1999b).

Radon concentrations in 56 percent of the 95 ground-water samples analyzed for radon were greater than 300 pCi/L (picocuries per liter), the USEPA proposed standard for drinking water. About 19 percent of the 95 samples exceeded 1,000 pCi/L (fig. 20). Two percent of the 95 samples exceeded the proposed Alternative Maximum Contaminant Level (AMCL) standard of 4,000 pCi/L. To comply with the AMCL, a State or local water utility must develop indoor air radon-reduction programs and reduce radon levels in drinking water to 4,000 pCi/L

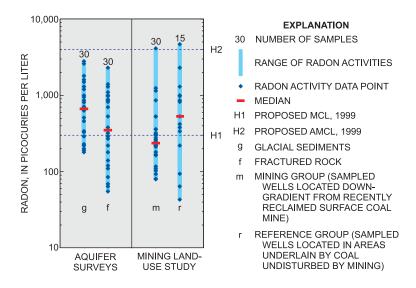


Figure 20. Radon concentration in ground water varied considerably within well groupings sampled in the Allegheny and Monongahela River

(U.S. Environmental Protection Agency, 1999b).

Large variation in radon concentration was found in ground water from the two aguifer systems sampled. Samples from wells in the valley-fill aquifers had a median radon concentration of 665 pCi/L; the median for samples from wells in the fractured-rock aguifers was 350 pCi/L. The higher radon concentrations in water of the valleyfill aquifers may be due to higher uranium content of the valley-fill deposits or may derive from the rock underlying these deposits. Samples from wells downgradient from recently re-claimed surface coal mines had a median radon concentration of 236 pCi/L. By comparison, water samples from wells in areas underlain by coal undisturbed by mining had a median radon concentration of 530 pCi/L. This difference may be due to several factors, such as (1) replacement of high-radon content overburden with lower-radon content backfill or (2) a greater release of radon directly to the air and less

entrapment in ground water after ground disturbance caused by surface mining.

Is radon a risk from your well?

The only way to be sure of radon concentration in ground water from a specific well is to have it tested. The U.S. Surgeon General recommends testing of indoor air radon levels in all homes (and apartments below the third floor). The USEPArecommended action level for indoor air radon levels is 4 pCi/L. The USEPA recommends testing well water for radon in homes where indoor air levels of radon are high. High concentrations of radon in well water can significantly contribute to airborne levels indoors. Although few of the 95 wells that were tested in ALMN had high concentrations of radon, the results show considerable variability (fig. 20). Ground water from each well should be checked if radon is a concern. If a large part of the indoor radon is from ground-water contribution, the USEPA recommends water treatment to remove radon.

REGIONAL STUDIES: Sulfate concentrations and biological communities in Appalachian coal areas indicate mining-related disturbances despite a general water-quality improvement between 1980 and 1998

In a 1998 study to assess regional water-quality effects of coal mining (Eychaner, 1999), samples representing the Northern Appalachian coal field were collected in the Allegheny and Monongahela River Basins (ALMN), where high-sulfur coal is common and acid mine drainage was historically severe, and samples for the Central Appalachian coal field were collected in the Kanawha-New River Basin (KANA), where acid drainage is uncommon (fig. 21).

Water chemistry in 178 wadeable streams was analyzed once during low streamflow in July and August 1998. Drainage area for most streams was between 4 and 80 mi². Most (170) of these stream sites were also sampled during a 1979–81 study on the effects of coal mining (Britton

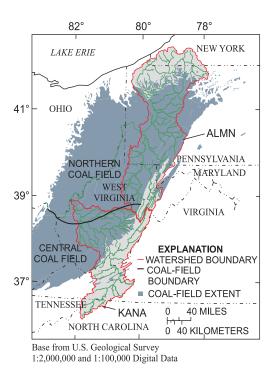


Figure 21. Coal-bearing rocks underlie 55 percent of the area sampled in the Northern and Central Appalachian bituminous coal fields. (Coal-field locations from Tully, 1996)

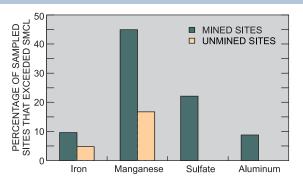


Figure 22. Stream water exceeded Secondary Maximum Contaminant Levels at mined sites more often than at unmined sites.

and others, 1989), before implementation of Surface Mine and Reclamation Control Act (SMCRA) Regulations began to affect regional water quality. At 61 sites, aquatic invertebrates (insects, worms, crustaceans, and

mollusks) also were collected. Ground water was sampled from 58 wells near coal surface mines and 25 wells in unmined areas.

Water-Quality Characteristics Targeted by SMCRA Improved in Streams, but Sulfate and Metals Remain High at Some Sites

Median pH increased and median total iron and total manganese concentrations in streams decreased among mined basins between 1979– 81 and 1998 in both coal fields, a reflection that these water-quality characteristics are regulated in mine discharges. Concentrations of sulfate, which is not regulated in mine discharges, exceeded regional background levels at sites downstream from mining (average of about 21 mg/L sulfate in

basins with no history of mining) in more than 70 percent of samples.

The highest sulfate concentrations were measured in basins with the greatest coal production. About one-fourth of all samples exceeded 250 mg/L, the USEPA Secondary Maximum Contaminant Level (SMCL) for drinking water, and all these exceedences were in mined basins (fig. 22). When coal mining ceases within a basin, sulfate concentrations gradually decrease (Sams and Beer, 2000).

Manganese, aluminum, and iron at stream sites in many mined basins also exceeded regional background concentrations (table 1). In the 1998 samples from the northern coal field, median total iron was about equal among mined and unmined basins; but in the central coal field, median total iron among mined basins was lower than among unmined basins. In both coal fields, median total manganese among mined basins was about double that among unmined basins. Exceedences of SMCLs for dissolved iron and manganese were more common in mined basins than in unmined basins, and the aluminum SMCL was exceeded in mined basins only.

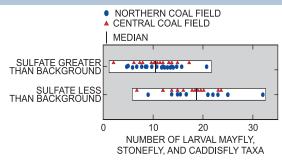


Figure 23. Sulfate concentration in stream water, an indicator of coal production in a basin, was inversely related to the number of mayfly, stonefly, and caddisfly taxa found at water-quality sampling sites.

Invertebrate-Community Impairment Appears Related to Amount of Mining

Invertebrate communities tended to be more impaired in mined basins than in minimally altered basins. Pollution-tolerant species were more likely to be present at mined sites than at unmined sites, whereas pollution-sensitive taxa were few or absent in heavily mined basins. Both an increased sulfate concentration and a decline in some aquatic-insect populations was related to coal production (fig. 23). At sites where sulfate concentrations were above the estimated background level (table 1), the number of taxa of three groups of sensitive insect species (mayflies, stoneflies, and caddisflies) was reduced, although the pH was 6.5 or greater at all these sites.

At the concentrations measured, the sulfate ion is relatively nontoxic to aquatic organisms and may not represent the cause of the decline in mayflies, stoneflies, and caddisflies observed. Sulfate is, however, related to the total coal production from a basin (Sams and Beer, 2000). Invertebrate communities may also have been impaired by other large-scale landscape disturbances—for example, changes

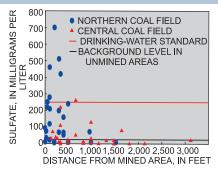


Figure 24. Sulfate concentrations in ground water generally exceeded regional background levels within about 1,000 feet from surface coal mines.

in hydrology, siltation, or tracemetal contamination, all of which can be caused by increased coal production. The communities in basins affected by low to moderate coal production were similar to communities in basins affected by urbanization, agriculture, large construction projects, flow alterations, or wastewater effluents.

Sulfate and Some Metal Concentrations were Higher in Ground Water near Surface Coal Mines

Sulfate concentrations in ground water generally were higher than regional background concentrations in shallow domestic watersupply wells within 1,000 feet of reclaimed surface mines (fig. 24). Water from such wells in the north-

ern coal field contained more sulfate and calcium than did wells in unmined areas in the same region, or at any of the sites in the central coal field. Iron, manganese, aluminum, magnesium, turbidity, and specific conductance also were higher than regional background concentrations within about 2,000 feet of reclaimed surface mines in both coal fields. Concentra-

tions of calcium and magnesium are higher near mined sites because these elements are components of minewater-treatment chemicals and of some of the rocks associated with coal seams. Ground water near reclaimed surface mines exceeded SMCLs for iron, manganese, sulfate, and aluminum more frequently than ground water in unmined areas (fig. 25). Iron and manganese occur naturally in native coal-bearing rocks, sometimes at high concentrations; however, nearly twice as many groundwater samples at mined sites exceeded SMCLs for iron compared to unmined sites. Wells where SMCLs for sulfate and manganese were exceeded were most commonly in the northern coal field.

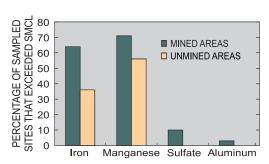


Figure 25. Ground water exceeded Secondary Maximum Contaminant Levels in mined areas more often than in unmined areas.